

PATENT ABSTRACTS OF JAPAN

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(54) FLUOROCOPOLYMER AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain the title copolymer having a low oligomer content and improved mechanical strengths by copolymerizing tetrafluoroethylene with a fluoro vinyl ether. CONSTITUTION: 90-99.5mol% tetrafluoroethylene is copolymerized with 10-0.5mol% fluorinated vinyl ether of the general formula: CF2=CFORf (wherein Rf is a halohydrocarbon group) and a shortstop is added to the reaction mixture. An unreacted monomer is removed from the mixture to obtain a fluorocopolymer having a specific melt viscosity of 102-107P as measured at 372° C and a weight loss of 0.01 wt.% or below when extracted with a fluoroorganic solvent.

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(— however, Rf is a halogenated hydrocarbon radical.) — the ratio which consisted of 10–0.5 mol % of monomeric units shown, and was measured at 372 degrees C — fluorine-containing copolymer characterized by for melt viscosity being 102–107poise, and the weight reduction by extract with a fluorine-containing organic solvent being 0.01 or less % of the weight. [Claim 2] General formula (1)

-IU-zCF2)- (I)
Less than [more than monomeric-unit 60 mol \$90 mol \$] and the general formula (II) which are been alike and based
[Formula 2]
- (CF2CF) - (II)
OR f

(--- however, Rf is a halogenated hydrocarbon radical.) — the ratio which exceeded ten mol % of monomeric units shown, consisted of less than [40 mol \$], and was measured at 200 degrees C — fluorine-containing copolymer characterized by for melt viscosity being 102-107poise, and the weight reduction by extract with a fluorine-containing organic solvent being 0.01 or less % of the weight. [Claim 3] Tetrafluoroethylene and the following general formula (III) CF2-CFORF (III)

CF2=CFORf (III)
(However, Rf is a halogenated hydrocarbon radical.) The manufacture approach of the fluorinecontaining copolymer according to claim 1 or 2 which is made to carry out copolymerization of
the fluorine-containing vinyl ether shown, and is characterized by removing an unreacted
monomer after adding a terminator.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application] This invention has few contents of the improved fluorine-containing resin, especially an oligomer component, and relates to the copolymer and its manufacture approach of the tetrafluoroethylene whose mechanical strength improved, and fluorine-containing vinyl ether. [0002]

on of the Prior Art) The copolymer (PFA is called hereafter.) of tetrafluoroethylene LUESCIPLOR OF THE PIPE ACT I HE CODONTMET (FFA IS CAUSED REPEATED OF GUIDENCHIPMEN PER PER ACT) OF GUIDENCHIPMEN SHE MEND WAS A BROOTCH'S HOUSE, CAN DE GUISEA, and is broadly used for costing, lining, etc. as mold goods, such as a tube, a pipe, a joint, and a container. Especially in the semi-conductor production process, it is widely used as an ingredient of piping, such as a wafer carrier, and a bottle or a tube, from the outstanding chemical resistance and thermal resistance.

[0003] [Proble

[0003]
[Problem(s) to be Solved by the Invention] However, also although it is called PFA, if it sees in a detail, it has some troubles. That is, PFA has comparatively much eluted particle compared with general-purpose resin, such as polyethylene, when it is used as the various containers or fixture for high accumulation LSI manufacture, it becomes the cause of yield aggravation, and so, reduction of particle is demanded strongly.

[0004] Since the rate of increase of a particle yield with time fell in the rare fluoric acid immersion test after chlorofluocarbon -113 extracts PFA, it is thought that one of the causes of the particle generated from PFA is oligomer contained in PFA. Then, washing of a PFA Plastic solid, fluorine gassing, and processing called the air purge at the time of shaping are tried as the approach of particle reduction, and, as a result, the amount of early embryogenesis of particle is reduced (the 2nd volume of ultra Clean Technology 456 and 453 pages, 1990). However, each of these approaches is surface processings, and since oligomer is eluted from the interior of resin with time, the actual condition is having not resulted in fundamental solution.

[Means for Solving the Problem] As a result of examining wholeheartedly fluorine-containing resin with few yields of particle, i.e., fluorine-containing resin with few oligonor components, by adding a terminator at the time of termination of a polymerization, this invention persons find out that very few fluorine-containing copolymers of an oligomer content are obtained, and came to complete this invention.

[0006] That is, this invention is a general formula (0. -(CF2CF2)- (f)

90-99.5 mol % and the general formula (II) of monomeric units which are been alike and based [0007]

[0008] (-- however, Rf is a halogenated hydrocarbon radical.) — the ratio which consisted of 10-

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general formula (II) among the fluorine-containing copolymers of this invention is % at 372 degrees C — melt viscosity serves as range which is 102-107poise, moreover, the ratio which the monomeric unit shown by said general formula (II) exceeded ten-mol %, and measured the copolymer which is less than [40 mol %] at 200 degrees C — melt viscosity serves as range which is 102-107poise, a ratio — when the moldability of a copolymer is taken into consideration in any case, as for melt viscosity, it is desirable that it is the range of 103-108poise.

[0018] Moreover, the fluorine-containing copolymer of this invention is JIS. The ***** breaking strength measured based on K-7113 is 250kg/cm2 or more, and it has sufficient physical properties also in the mechanical strength. The above-mentioned ***** breaking strength can also be made into 300 morekg/cm2 or more.

[0019] Furthermore, a fluorine-containing organic solvent can extract the oligomer contained in the fluorine-containing copolymer of this invention, and it can carry out a quantum by weight reduction after an extract in a fluorine-containing organic solvent for 80 degrees C and 18 hours. The weight percentage reduction when being extracted by the fluorine-containing organic solvent is 0.01 or less % of the weight, and can also make the fluorine-containing copolymer of this invention 0.08 more or less % of the weight.

[0020] The well-known organic solvent which has a fluorine atom can be used for the fluorine-containing organic solvent which can be suitably used especially in this invention is illustrated concretely. CFCIZCFZCI (chlorofluocarbon – 141b) can be raised, for example.

[0021] When the weight percentage reduction of the fluorine-containing organic solvent which can be suitably used especially in this invention is illustrated concretely. CFCIZCFZCI (chlorofluocarbon – 133) and CH3CCIZF (chlorofluocarbon – 141b) can be raised, for example.

[0021] When the weight percentage reduction of the fluorine-containing orgophymer of this invention is ver

oligomer component. [0022] The fluorine-containing copolymer of this invention can check the chemical structure by measuring an infrared absorption spectrum (only henceforth IR). Namely, when the inside of the monomeric unit shown by said general formula (II) and Rf are perfluoroalkyl radicals, It has the absorption band based on a ~CF2-radical in a >CFOCF2-radical and the 1200cm-1 neighborhood. Moreover, in the case of the radical Rf is indicated to be by said general formula (IV), it has the ebsorption band based on a ~CH2-radical in a >CFOCH2-radical and the 2900cm-1 neighborhood to the 950cm-1 neighborhood among the monomeric unit shows by said general formula (II). by said general formula (II).

by sale general formula (u).

(D023) Although the fluorine-containing copolymer of this invention may be manufactured by what kind of approach, it is suitably manufactured by the approach stated to especially a degree.

(D024) Namely, tetrafluoroethylene and the following general formula (III) CF2=CFORf (III)

Orzero On tau. (However, Rf is a halogenated hydrocarbon radical.) After carrying out copolymerization of the fluorine-containing vinyl ether shown and adding a terminator, it is the approach of removing an

urvacated monomer.

[0025] The same radical as Rf in said general formula (II) can be used for the halogenated hydrocarbon radical shown by Rf in said general formula (III). If the fluorine-containing vinyl ether shown by the general formula (III) and by this invention is illustrated concretely CF2=CF0CH2CF2-CFCOCH2CF2-CF3. CF2=CF0CH2CF2-CF4 CF2=CF0CH2(CF2)2CF3. CF2=CF0CH2(CF2)3CF3. CF2=CF0CH2(CF2)3CF3. CF2=CF0CH2(CF2)3CF3. CF2=CF0CH2(CF2)3CF3. CF2=CF0CH2(CF2)3CF3. CF2=CF0CH2(CF2)3CF3. CF2=CF0CH2(CF2)3CF2. CF2=CF0CH2)3CF2. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF3. CF2=CF0CH2)3CF2. CF2=CF0CH2)3CF2. CF2=CF0CH2. CF2=C

8CF3 grade can be reised.
[0026] The preparation presentation of the fluorine-containing vinyl ether shown by tetrafluoroethylene and said general formula (III) in this invention in order to seldom enlarge melt

0.5 mol % of monom containing copolymer reduction by extract w own, and was measured at 372 degrees C — it is the fluorine-zed by for melt viscosity being 102-107poise, and the weight vine-containing organic solvent being 0.01 or less % of the weight.

(0009) Moreove -(CF2CF2)- (I) ver, this invention is a general formula (I).

Less than [more than mor omeric-unit 60 mol \$90 mol \$] and the general formula (II) which are

(0010) [Formula 4] - (CF₂CF) m **or**

[0011] (— however, Rf is a halogenated hydrocarbon radical.) — the ratio which exceeded ten mol % of monomeric units shown, consisted of less than [40 mol %], and was measured at 200 degrees C — it is the fluorine-containing copolymer characterized by for melt viscosity being 102–107poise, and the weight viscosity being the state of the maintain of the property of the property

inc-in/poise, and the weight reduction by extract with a fluorine-containing organic solvent being 0.01 or less % of the weight. [0012] The monomeric unit shown by said general formula (I) is a monomeric unit based on the polymerization of tetrafluoroethylene. [0013] Setting the radical shown by Rf emong the monomeric unit shown by said general formula (II) especially to this invention, although a halogenated hydrocarbon radical is generally used, a suitable radical is a perfluoroallyl radical and the following general formula (IV).

-CH2CaFbXcH(Za+I-b-c) (IV)

(— however, X is a chlorine atom or a bromine atom, a is one or more integers, b is the integer of 0-2a+1, and c is 0 or 1, and it has the relation of 1 (=b+c(=2a+1,) — it is the radical shown. Although especially the carbon number of the halogenated hydrocarbon radical shown by Rf is not restricted, it is desirable that they are carbon numbers 1−8 from the ease of acquisition of a material.

not restricted, it is desirable that they are carbon numbers 1-8 from the case of acquisition of a raw material.

(0014) In this invention, also in the monomeric unit shown by said general formula (II), when Rf is a general formula (IV), since the content of oligomer has good **** breaking strength few, the fluorine-containing copolymer of this invention is suitable. This reason can be considered that it is because the generation prevention effectiveness of the oligomer component in a monomer clearance phase is large since the monomer whose Rf is a general formula (IV) has polymerization nature better than the monomer which is a perfluoreably radical in the manufacture approach of the fluorine-containing copolymer of this invention mentioned later. (0015) The unit the presentation of each monomeric unit shown by said general formula (II) and (II) is indicated to be by said general formula (II) is 60 – 99.5-mol %, and the unit shown by said general formula (III) is 40 – 0.5-mol %. When there are few amounts of the monomeric unit shown by said general formula (III) has below-mentioned range, since melt viscosity becomes high too much and it becomes a copolymer with a bad moldability, and softening temperature falls when [than the above-mentioned range is nice effectively in the problem generates and is not desirable to a moldability. When the moldability of the fluorine-containing copolymer of this invention is taken into consideration, as for the monomeric unit shown by said general formula (I) and (III), it is desirable respectively that it is [75 – 99.5 mol / 25 – 0.5 mol / 3 and | 3 knrther respectively.

[0016] The fluorine-containing copolymer of this invention is insoluble to various solvents, molecular weight cannot be calculated with the usual means, however, the ratio of the fluorine-containing copolymer of this invention is insoluble to various solvents. molecular weight cannot be calculated with the usual means, however, the ratio of the fluorine-containing copolymer of this invention = since melt vi

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viscosity of the fluorine-containing copolymer obtained, and to maintain softening temperature to a suitable value and to make a fabricating operation easy The fluorine-containing vim) other shown by said general formula (III) 0.5-40-mol %, it is desirable that the 99.5-60-mol range of tetrafluoroethylene is %, and it is still more desirable that the fluorine-containing vinyl ether shown by said general formula (III) is 0.5-25-mol %, and the 99.5-75-mol range of

shown by said general formula (III) is 0.5-25-mol %, and the 99.5-75-mol range of tetrafluoroethylene is %.

[0027] Furthermore, in order to reform the property of the copolymer obtained again, fluoro olefins, such as hazafluoropropylene, chlorotrifluoroethylene, and vinylidene fluoride, may be added to tetrafluoroethylene. these — general — tetrafluoroethylene — receiving — less than [5 mol %] — using is desirable.

[5 mol %] — using is desirable.
[O028] Next, a well-known approach [have / especially / the approach of copolymerization of the above-mentioned fluorine-containing vinyl ether and tetrafluoroethylene / a limit] is adopted. Namely, what is necessary is to adopt the approach of arbitration, such as a solution polymerization method, and an emulsion-polymerization method, and just to choose the optimal polymerization method according to conditions of a

method, and just to choose the optimal polymerization method according to conditions of a monomer, such as copolymeric.

[0029] Among these, first, if a solution polymerization method is explained concretely, although especially definition is not carried out for the polymerization solvent used, generally chlorofluorocarbon, a chloro fluoro hydrocarbon, perfluorocarbon, etc. will be used suitably. Moreover, in the case of solution polymerization, it is also possible in a polymerization solvent 0.3 to 10 time weight and to make the water of weight live together one to 5 times preferably, and to carry out a polymerization because of clearance of the heat of polymerization.

[0030] Moreover, although a well-known radical generating agent is employable as a polymerization initiator, when the thermal resistance of the copolymer obtained is taken into consideration, a fluorine-containing radical generator is desirable. [Z(CF2) yCO2] 2 (however, Z is a hydrogen atom, a fluorine atom, or a chlorine atom, and y is the integer of 1–5.)

[Formula 5]

[Formula 5]
[Z (CF₂) , (OCFCF₂) , OCFCO₂) ₂
CF₃ CF₃

[0032] (— however, Z is a hydrogen atom, a fluorine atom, or a chlorine atom, y is the integer of 1–5, and q is the integer of 0–3.) — it can be used suitably. If the example of the radical generating agent suitably used in this invention is shown, it will be 2 (HCF2CF2CO2). 2 (CF3CF2CF2CO2). 2 (CF3CF2CF2CO2). 2 (CF3CF2CF2CO2). and [0033]. [Formula 6] (CF3CF2CF2OCFCO2) 2

ĊF₃

things are made

[0034] ******** — things are made.
[0035] the amount of monomers usually used although the amount of the above-mentioned radical generating agent used cannot generally be *******(ed) with the solvent to be used, polymerization conditions, especially temperature — receiving — 0.002-0.5-mol % — what is necessary is just to choose out of the 0.005-0.2-mol range of % preferably Moreover, a radical generating agent may be collectively introduced at the time of polymerization initiation, and may be intermittently introduced during a polymerization. Especially the thing for which a radical generating agent is again added on the way in such a case although a polymerization may be unable to progress easily the middle depending on conditions is an effective means.
[0036] Although polymerization temperature is decided considering the catabolic rate of the radical generating agent to be used as one rule of thumb, 0-100 degrees C is usually 5-60 degrees C preferably.
[0037] Next, a suspension polymerization is explained. The polymerization initiator in a suspension polymerization, its amount used, and polymerization temperature can be carried out

like the above-mentioned solution polymerization. It is desiral a suspension polymerization. Although a thing well-known a that there is no limit in any way, the perfluoro carboxylic-ad use a distributed stabilizer in uted stabilizer is adopted um with which perfluor carboxylic-acid ammonium, perfluoro sulfonic-acid ammonium, pinyl alcohol, etc. are used, and a carbon number has the long-chain alkyl group of 5-10 from especially the effectiveness of distributed stability and the point of the thermal stability of the obtained fluorine-containing

distributed stability and the point of the thermal stability of the obtained fluorine-containing copolymer is suitable. Moreover, the chlorofluorocarbon and perfluorocarbon other than the above-mentioned distributed stabilitizer may be used from a viewpoint of distributed stability, and 0.1 to 1 time weight is suitable for the amount to water. [0038] Furthermore, if an emulsion polymerization is explained, in an emulsion polymerization, a meltable radical generating agent will be used for water as a polymerization initiator, and inorganic peroxides, such as ammonium persulfate and potassium persulfate, will usually be used suitably, 20-140 degrees C of polymerization temperature are 40-100 degrees C preferably, an emulsion polymerization— it may be, or a distributed stabilizer may be used and the class and amount are as the above-mentioned suspension polymerization having explained. Furthermore, using buffers, such as an ammonium carbonate, in an emulsion polymerization does not have inconvenience in any way, either.
[0039] If the pressure of tetrafluoroethylene is the range of 1-30kg/cm2-G also in which polymerization method, a polymerization reaction will fully advance, but in a not much high-pressure case, since the fault which becomes quite [in equipment] expensive arises, 1-10kg/cm2-G is usually desirable.

10kg/cm2-G is usually desirable.

pressure case, since the fault which becomes quite [in equipment] expensive arises, 110kg/cm2-G is usually desirable.

[0040] About supply to the polymerization tank of the above-mentioned monomer component,
the tetrafluoroethylene and fluorine-containing vinyl ether of the specified quantity may be
confined in a polymerization tank, and a polymerization may be performed, and
tetrafluoroethylene, fluorine-containing vinyl ether, or both may be added continuously or
intermittently during a polymerization according to the consumption by the polymerization of
tetrafluoroethylene and fluorine-containing vinyl ether.

[0041] Furthermore, it is desirable to add the chain transfer agent of an initial complement also
in which polymerization method for molecular weight accommodation. As a chain transfer agent,
although alcohols, such as either; methanols, such as a slanes; diethylether, such as chlorinatedhydrocarbors; hexanes, such as a carbon tetrachloride and chloroform, a pentane, butane, a
propane, ethane, and methane, and wood ether, and ethanol, can be used, the alkanes from a
preason and alcohols, such as the amount of dissolutions to a polymerization solvent and the
stability of the generated cooplymer, are [among these] desirable. What is necessary is just to
press fit by the pressure which can maintain the required amount of dissolutions to a
polymerization solvent, if a chain transfer agent is a gas, moreover— if it is a liquid — an initial
complement — beforehand — or what is necessary is just to add intermittently Although the
amount of the chain transfer agent used is changed in some range according to the class of
chain transfer agent, and polymerization conditions, 0.05-10-mol % and a thing [the 0.1-5 mol
range of %] preferably are usually desirable to the total amount of monomers in a polymerization
tank. When water exists in a polymerization system here, it is desirable to make it addition in
consideration of the partition ratio of the aqueous phase of a chain transfer agent and an organic
ph

phase, so that the concentration of the chain transfer agent in an organic phase may serve as the above-mentioned range.

[0042] In the approach of this invention, a terminator is added and a polymerization reaction is stopped, after performing the above-mentioned copolymerization. Especially, it is not restricted but a terminator can be used, if it is the compound which can be made to suspend a polymerization reaction substantially. Phenols, such as quinones; hydroquinones, such as polymerization reaction substantially. Phenols, such as a quinones; hydroquinones, such as the terpenes; benzoquinones, such as a shorinated-hydrocarbons; innonens, such as hydrocarbons; carbon tetrachlorides, such as alcohols; hexanes, such as a methanol and ethanol, a pentane, and butane, and chloroform, a cymenc, and a pinene, and a naphthoquinone, cresol, and a catechol, can be used, among these, specifically, alcohols, hydrocarbons, and chlorinated hydrocarbons are suitable by the reasons of the thermal stability of the effectiveness of a polymerization reaction halt, separation from a fluorine-containing copolymer, and the obtained fluorine-containing copolymer, and the obtained fluorine-containing halt, separation from a fluorine-containing copolymer, and the obtained fluorine-containing

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[0051] Moreover, the fluorine-containing copolymer of this invention is excellent in mechanical [0051] Moreover, the fluorine-containing copolymer of this invention is excellent in mechanical physical properties, and from the copolymer of the same presentation manufactured by the conventional approach, and the same ratio melt viscosity, it has **** breaking strength usually high 30-60kg/cm2, and it can be said that this invention is excellent also from this point. [0052] Therefore, when it uses for piping systems, such as a wafer carrier, and a bottle or a tube in a semi-conductor production process, the fluorine-containing copolymer of this invention has few yields of particle, and can be used in the industrial field as which properties as a fluororesin, such as chemical resistance, thermal resistance, and an electrical property, are required as a fluorine-containing copolymer by which it is not only effective, but mechanical strength was improved in manufacture of the high accumulation LSI. [0053] [0053]

[Example] Although an example is shown below in order to explain this invention to a detail

[0053] Although an example is shown below in order to explain this invention to a detail further, this invention does not receive a limit at all according to these examples. [0054] In addition, measured value was calculated as follows. [0056] I. Measurement JIS of ***** breaking strength it is based on K-7113. [0056] b. By fusing the resin for the fluorine-containing copolymer of creation this invention of a test sample, and a comparison at the temperature of 350 degrees C, and cooling under application of pressure, the sheet of Imm thickness was created and the test piece required for the above-mentioned examining method was created. [0057] 2. a ratio — the measurement high-rized type flow tester of melt viscosity was used. After high grade isopropyl alcohol and ultrapure water having repeated and washed the measurement test piece of the 3.a. particle measured by the 13.14kg load with the temperature of 372 degrees C using the dice with a diameter [of Imm], and a die length of 10mm and making it season naturally in a clean room, it was immersed in 500g of 50% fluoric acid solutions of high grades, and aging of the number of particle was measured. In addition, for measurement, the number of particle of 0.3-2 micrometers was counted using particle counter KL-22 (Rion make). [0058] b. By fusing the resin for the fluorine-containing copolymer of creation this invention of a test sample, and a compurison at the temperature of 350 degrees C, and cooling under application of pressure, the sheet of Imm thickness was created, it started to 50mmx70mm and the test piece required for the above-mentioned trial was created. [0059] Chlorofluocarbon -113 beforehand refined by distillation to 75L reactor made from stainless steel with example 1 agistor After putting in 45kg, the interior was deserted and it considered as atmospheric pressure with nitrogen gas after that. After putting in methanol 8.0g and 2. 2, 3 and 3, and 3-pentafluoro propyl trifluoro vinny ether 320g in a reactor, the engine speed of a stirring motor was

12 hours, the 2kg copolymer was obtained. [0060] This fluorine-containing copolymer was film-ized at 330 degrees C. IR was measured, and that result was shown in drawing 1, the monomeric unit based on [in drawing 1, the absorption band based on a ~CH2-radical is checked by a >CFOCH2-radical and the 2900cm-1 neighborhood to the 950cm-1 neighborhood, and] 2, 2, 3, 3, and 3-pentafluoro propyl trifluoro vinyl ether to the inside of a fluorine-containing copolymer ~ 2.8-mol \ ~ — it turned out that it is contained. Moreover, melting shaping of this polymer is carried out, and it is JIS. It was 440kg/cm2 when **** breaking strength was measured based on K-7113, moreover, a 372-degree C ratio — melt viscosity was 1.5x105poise.
[0061] Furthermore, 1kg of this polymer was put into the autoclave of capacity 3L, and the

copolymer etc. [0043] Although it is monomers which remain cohymerization system, although the addition of a terminator cannot generally be *******(ed) with the effectiveness of a polymerization method and the terminator to add etc., its the 20-300-mol range of % is desirable from the effectiveness of a polymerization reaction halt, a viewpoint [terminator / the fluorine-containing copolymer of this invention, and] of separation, etc.

[0044] In addition the viewpoint [is usually used exceeding ter-mol 5 to the amount of unreacted

[0045] If it is the addition stage of a terminator and it is in the condition that the unreacted monomer remains in a polymerization system after a polymerization reaction starts, it is effective in every phase. However, if it is the initial stage of a polymerization reaction starts, it is effective in every phase. However, if it is the initial stage of a polymerization unch, it is inconvenient from a viewpoint of the productivity of a fluorine-containing copolymer, and when a polymerization reaction progresses not much and a polymerization system becomes hyperviscosity, uniform stirring may become difficult, as a result, clearance of the heat of polymerization may serve as imperfection, and it may have an adverse effect on the physical properties of the copolymer obtained. Therefore, although what is necessary is just to determine the addition stage of a terminator from a viewpoint of the physical properties of a fluorine-containing copolymer, and productivity acquired, it is usually desirable that it is an event of the concentration of the fluorine-containing copolymer in reaction mixture serving as 3 - 20% of the weight of range preferably two to 30% of the weight. [0046] Moreover, the approach the addition approach of a terminator fit in a polymerization system although especially definition is not carried out, and polymerization reaction liquid to the container containing a terminator, the approach of introducing a terminator immediately after depressuring by bleedoff of unreacted tetrafluoroethylene, etc. are mentioned as an example.

introducing a terminator immediately after depressuring by bleedoff of unreacted tetrafluoroethylene, etc. are mentioned as an example.

[0047] In this invention, an unreacted monomer is removed after addition of a terminator. Clearance of an unreacted monomer is removing at least unreacted tetrafluoroethylene and one side of unreacted fluoro alkyl vimyl other, and the actuation can adopt the well-known monomer clearance approach. For example, actuation in which means, such as filtration, centrifugal separation, heating, and reduced pressure, separate the unreacted tetrafluoroethylene and unreacted fluoro alkyl vinyl other which dissolved into the actuation to which gas tetrafluoroethylene is made to emit, and a polymerization sphere with a fluoroethylene is made to emit, and a polymerization sphere with a fluoroethylene is made to emit, and a polymerization sphere with a fluoroethylene is made to emit, and a polymerization sphere with a fluoroethylene is made to emit, and a polymerization sphere with a fluoroethylene is made to emit. unreacted fluoro alkyl vinyl ether which dissolved into the actuation to which gas tetrafluoroethylene is made to emit, and a polymerization solvent with a fluorine-containing copolymer etc. can be raised from the gaseous phase of a polymerization tank. [0048] The generated fluorine-containing copolymer separates an unreacted monomer, a solvent, an excessive terminator, etc. and is obtained from polymerization reaction mixture. [0049] By fluorinating using a fluorination agent, F2 [for example,], what has a hydrogen atom in intramolecular among the fluorine-containing copolymers of this invention can be fluorinated by high yield, without causing cutting of the principal chain accepted by fluorination of the conventional hydrocarbon polymer, and can be used as a perfluoro copolymer. [0050]

[Effect of the Invention] When the particle which is immersed in fluoric acid and generates the [Effect of the Invention] When the particle which is immersed in fluoric acid and generates the fluorine-containing copolymer of this invention is measured, there are not only very few early yields, but after time amount progress does not increase. Moreover, chlorofluocarbon – 113 and chlorofluocarbon – There is very little weight reduction when fluorine-containing organic solvents, such as 141b, extract as 0.01 or less % of the weight. From this, it can be said that the fluorine-containing copolymer of this invention has very few contents of an oligomer component. Moreover, although it is thought that the component which causes particle besides an oligomer component is contained in a fluororesin, since the particle yield of the fluorine-containing copolymer of this invention is very low, it is thought that a component which causes particle other than such oligomer is also reduced. other than such oligomer is also reduced.

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extract was performed at 80 degrees C for 18 hours, 1L Using chlorofluocarbon -113 and chlorofluocarbon-141b respectively. After filtration separated the copolymer and the solvent, reduced pressure drying of the copolymer was carried out at 150 degrees C for 12 hours. Weight reduction of the copolymer at this time was 0.004 % of the weight in chlorofluocarbon-141b 0.004% of the weight by chlorofluocarbon-113 Moreover, when the chlorofluocarbon-113 used for the extract was condensed, the 0.04g white matter was obtained. [0062] After the example of comparison I reactor pressure became 2.6kg/cm2, the unreacted monomer and the solvent were made to distill, without adding a methanol, and also it reacted like the example 1, the monomeric unit based on 2, 2, 3, 3, and 3-pentafluoro propyl trifluoro vinyl ether in the inside of the copolymer obtained as a result of analysis — 2.8-mol % — it was contained, moreover, **** breaking strength — 380kg/cm2 — it is — a ratio — melt viscosity was 1.4x105poise, and the weight reduction after an extract was 0.05 % of the weight by chlorofluocarbon —113 extracted an in the thermore, when chlorofluocarbon —113 extracted an interest of the copolymer obtained as a result of the copolymer obtained as a result of analysis — 2.8-mol % — it was contained, moreover, **** breaking strength — 380kg/cm2 — it is — a ratio — melt viscosity was 1.4x105poise, and the weight reduction after an extract was 0.05 % of the weight by chlorofluocarbon —113 extracted — it is — a return of the copolymer obtained as a result of analysis — 2.8-mol % — it was contained.

was 1.4x105poise, and the weight reduction after an extract was 0.05 % of the weight by chlorofluocarbon –113.

(10083) Furthermore, when chlorofluocarbon –113 extracted again the copolymer extracted by chlorofluocarbon –113, weight reduction was 0.025 % of the weight. Moreover, the weight reduction by the extract by chlorofluocarbon –1141 bof this copolymer was 0.05 % of the weight. (10084) Chlorofluocarbon –113 beforehand refined by distillation to 75L reactor made from stainless steel with example 2 agitator After putting in 70kg, the interior was deserated and it considered as atmospheric pressure with nitrogen gas after that. After putting in methanol 37g and perfluore propyl vinyl ether 8.2kg in an autoclave, the engine speed of a striving motor was considered as 140 rotations, totrafluoroethylene was introduced and the pressure was set to 5kg/cm2–G. Subsequently, keeping the inside of a reactor at 18 degrees C, 180g (5wt%) of 6hlorofluocarbon –113 solutions of 2 was introduced, and the polymerization was started (C3F7CO2). Tetrafluoroethylene was continuously supplied so that a reactor pressure might maintain 6kg/cm2–G. It moved to the polymer deposit tub of 100L which has the agitator into which methanol 1 kg went reaction mixture in the place where the concentration of the fluorine-containing copolymer which 3.9kg of amount of supply of tetrafluoroethylene generated became 5.7h of the weight into reaction mixture, and the polymerization was stopped. Next, by heating a polymer deposit tub, the solvent and the unreacted monomer were made to distill and the copolymer was obtained.

(2065) The absorption band based on a ~CF2-radical was checked by a >CFOCF2-radical and the 1200cm-1 neighborhood to the 990cm-1 neighborhood, and IR measurement showed that the content of the monomeric unit based on the perfluoro propyl vinyl ether of this copolymer was 1.3-mol % moreover, *** breaking strength — 410kg/cm2 — it is — a 372-degree C ratio — melt viscosity was 8 0x104poise, and the weight reduction after an extra

[U080] A methanol was not put into the example of comparison 2 polymer deposit tub, and also it reacted like the example 2: the content of the monomeric unit based on the perfluoro propyl vinyl other of this copolymer the result of analysis — 1.3-mol % — it is — a 372-degree C ratio — melt viscosity was 8.7x104poise, and the weight reduction after an extract of **** breaking strength was 0.06 % of the weight by 370kg/cm² and chlorofluocarbon -113.

[10067] The copolymer after chlorofluocarbon –113 extracts the fluorine-containing copolymer obtained in example 3 examples 1 and 2 and the examples and 2 of a comparison was immersed into 50% fluoric acid, and the number of particle of 0.3-2 micrometers in one cc of fluoric acid, and the number of particle of 0.3-2 micrometers in one cc of fluoric acid, and the number of particle of 0.3-2 micrometers in one cc of

fluoric acid solutions was measured 6, 9, and 14 days after immersion initiation. The result was [0068]

(A table 1)

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	表1		
	パーティクル	数(個/cc-	ファ政治を
	5 H th	9 H We	1488
突施例1	8	8	8
比較例 1 (1回目70/抽出度)	390	5 2 5	700
比較例 1 (1回目70/抽出後)	9 8	138	177
実施例 2	14	1 4	14
比較何2	203	310	3 9 5

[0069] Chlorofluocarbon -113 beforehand refined by distillation to 75L reactor made from [0069] Chloroflucarbon -113 beforehand refined by distillation to 75L reactor made from stainless steel with example 4 agitator After putting in 45kg, the interior was deserated, the mixed gas of the nine-mol % 2, 2, and 2-brifluoro eithy trifluoro vinryl ether, and 91-mol % of the tetrafluoroethylene which were prepared beforehand after that was introduced into the reactor, and it considered as atmospheric pressure. After putting in methanol 24g in a reactor, the rotational frequency of a stirring motor was considered as 140 revolutions, and the abover-mentioned mixed gas was introduced and it was made 4,0kg/cm2-G. Subsequently, keeping the inside of a reactor at 22 degrees C. 90g (5wt%) of chlorofluoration -113 solutions of 2 was introduced, and the polymerization was started (C2F5CO2). The account mixed gas of reaction Nakagami was introduced continuously, and 4,0kg/cm2-G was maintained. After putting in hexane 1kg in the place where the concentration of the fluorine-containing copolymer which the 3,0kg of the amounts of installation of the abover-mentioned mixed gas generated became 6.7% of the weight into reaction mixture and stopping a polymerization, the copolymer was obtained like the example 1.

[0070] The monomeric unit based on 2, 2, and 2-trifluoro ethyl trifluoro vinyl ether which the

[0070] The monomeric unit based on 2, 2, and 2-trifluoro ethyl trifluoro vinyl ether which the absorption band based on a ~CHZ-radical is accepted in the 950cm-1 neighborhood to a XCFOCHZ-radical and the 2900cm-1 neighborhood, and is contained in a copplymer like an example 1 as a result of IR measurement was 8.8-mol 5, moreover, a ratio — melt viscosity was 8.0×103poise, ***** breaking strength was 330kg/cm2, and weight reduction was 0.005 % of the weight as a result of the extract with chlorofluocarbon ~113.
[0071] After putting perfluoro tributylamine 15kg beforehand refined by distillation, and C7F15CO2NH4100g 21kg of ion exchange water into 75L reactor made from stainless steel with example 5 agitator, the interior was deserated, the mixed gas of the three-mol % the 2, 2, 3, 3, and 3-pentafluoro propyl trifluoro vinyl ether, and 97-mol % of the textifluoroethylene which were prepared beforehand after that was introduced into the reactor, and it considered as atmospheric pressure. After putting in ethanol 5kg in a reactor, the rotational frequency of a stirring motor was considered as 140 revolutions, and the abover-mentioned mixed gas was introduced and it was made 4.0kg/cm2-G. Subsequently, keeping the inside of a reactor at 18 degrees C, 25tg (5wt%) of perfluoro tributylamine solutions of 2 was introduced, and the polymerization was started (CICF2CF2CO2). The account mixed gas of reaction Nakagami was introduced continuously, and 4.0kg/cm2-G was maintained. After putting in chloroform 1kg in the introduced continuously, and 4.0kg/cm2-G was maintained. After putting in chloroform 1kg in the place where the concentration of the fluorine-containing copolymer which the 2.5kg of the amounts of installation of the above-mentioned mixed gas generated became 6.9% of the weight into reaction mixture and stopping a polymerization, the copolymer was obtained like the example

[0072] The monomeric unit based on the 2, 2, 3, 3, and 3-pentafluoro propyl trifluoro vinyl ether which the absorption band based on a -CH2-radical is accepted in the 950cm-1 neighborhood to

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web_cgi_eije

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Į				,				
	47.46	4	第一位 中國	(7)-张1.31-90 比陷的税底	比松的特征	8	747 118/8/118	N-7195E
		15	3	おもつへを成み 単位(mol%)	(ポイズ)	(kg/ca*)	たける関数は大きの関数	(48/cc)
-	CPCPOCH,CP.CF.B	E8,98	1200	2.2	2.0×10*	460	0.001	LO.
8	CF, CFOCH, (CP,), CP,	C, II. 4	2000	9 . 9	1.2×10*	350	0.004	-
ო	CF.*CFOCII,(CF.),CF.	CHC1.	0001	8 . 8	5.2×10³	320	800.0	
7	CP,*CPOCII,(CP,),CF,	. B	150	. es	1. 4×10*	360	0.005	
5	CP.+CP0CII,CP,CP,C1	CU,081 1000	0001	9.0	1.2×10*	350	0.004	-
9	CF.*CFOCU.CF,CF,CI	8,10	900	1.2	9.5×10**	320	0.007	-
۲	CP, CFOCH,CP,CF,C1	CII,04I	80	2.1	3.3×10**	300	0.009	2.1
Œ.	件) * 印は200℃で資定した比冷磁化すであり、それ以外は372℃で耐定した比溶酸粘度である。	开路路等	4.58.9	. thunhus 7	2℃で耐定し	た比容器品	CT65.	

[Translation done.]

a >CFOCH2-radical an example 1 as a result surement was 2.8-mol % moreover, a ratio — melt viscosity was 2.8-mol %. moreover, a ratio — melt viscosity was 450kg/cm2, and weight rate reduction was 0.003 % of the weight as a result of the extract by chlorofluocarbon – 113.

[0073] Using the same approach as example 8 examples 1 and 2, various fluorine-containing vinyl ether and the reaction of tetrafluororethylene were performed, and the fluorine-containing copolymer was obtained, the content of the monomeric unit based on the fluorine-containing vinyl ether contained in the class of used fluorine-containing vinyl ether, the terminator, and the obtained copolymer, and the ratio of the obtained copolymer — the number of particle after immersion was shown in a table 2 for 14 days at melt viscosity, *** breaking strength, the "weight percentage reduction by extract with chlorofluocarbon — 113, and 50% fluoric acid. (0074) The absorption band based on a ~CH2-radical was accepted in the 950cm—1 neighborhood to a >CFOCH2-radical and the 2900cm—1 neighborhood like [any copolymer] the example 1 as a result of IR measurement. [A table 2]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[<u>Orawing 1</u>] <u>Drawing 1</u> is the chart of the infrared absorption spectrum of the fluorine-containing copolymer of this invention.

[Translation done.]

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05/09/08

FLUOROCOPOLYMER AND ITS PRODUCTION

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Applicant:

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C08F214/26

- european:

Application number: JP19920234930 19920902 Priority number(s): JP19920234930 19920902

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Abstract of JP6080733

PURPOSE:To obtain the title copolymer having a low oligomer content and improved mechanical strengths by copolymerizing tetrafluoroethylene with a fluoro vinyl ether. CONSTITUTION:90-99.5mol% tetrafluoroethylene is copolymerized with 10-0.5mol% fluorinated vinyl ether of the general formula: CF2=CFORf (wherein Rf is a halohydrocarbon group) and a shortstop is added to the reaction mixture. An unreacted monomer is removed from the mixture to obtain a fluorocopolymer having a specific melt viscosity of 10<2>-10<7>P as measured at 372 deg.C and a weight loss of 0.01wt.% or below when extracted with a fluoroorganic solvent.

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(54)【発明の名称】 含フッ素共重合体およびその製造方法

(57)【要約】

【目的】オリゴマー成分が少なく、機械的強度の向上さ れた含フッ素樹脂を提供する。 【構成】一般式(Ⅰ)

$$-(CF_1CF_1) -$$

(I)

に基づく単量体単位60~99.5モルおよび一般式 (II)

[{{\text{t} 1}}

(但し、Rfはハロゲン化炭化水素基である。)で示さ れる単量体単位、例えば、2,2,3,3,3-ペンタフルオロブ ロピルトリフルオロビニルエーテルに基づく単量体単位 40~0.5モル%からなり、比溶融粘度が102~1 0'ポイズであり、含フッ素有機溶媒での抽出による重 量減少が0.01重量%以下である含フッ素共重合体。

【特許請求の範囲】

【請求項1】一般式(1)

 $-(CF_1CF_1) -$

(1)

に基づく単量体単位90~99. 5 モル%および一般式 (II)

【化1】

(但し、Rfはハロゲン化炭化水素基である。)で示さ 10 れる単量体単位10~0.5モル%からなり、372℃で測定した比溶融粘度が10²~10′ポイズであり、含フッ素有機溶媒での抽出による重量減少が0.01重量%以下であることを特徴とする含フッ素共重合体。

【請求項2】一般式(I)

$$-(CF_1CF_1) -$$

(I)

に基づく単量体単位60モル%以上90モル%未満および一般式(II)

【化2】

(但し、Rfはハロゲン化炭化水素基である。)で示される単量体単位10モル%を越え40モル%以下からなり、200℃で測定した比溶融粘度が10²~10°ポイズであり、含フッ素有機溶媒での抽出による重量減少が0.01重量%以下であることを特徴とする含フッ素共重合体。

【請求項3】テトラフルオロエチレンと下記一般式(II I)

 $CF_{i} = CFORf$

(III)

(但し、Rfはハロゲン化炭化水素基である。)で示される含フッ素ビニルエーテルを共重合させ、重合停止剤を添加した後未反応モノマーの除去を行うことを特徴とする請求項1または請求項2記載の含フッ素共重合体の製造方法。

【発明の詳細な説明】

[0001]

【産業上の利用分野】本発明は、改良された含フッ素樹脂、特にオリゴマー成分の含量が少なく、機械的強度の 40向上されたテトラフルオロエチレンと含フッ素ビニルエーテルの共重合体およびその製造方法に関する。

[0002]

【従来の技術】テトラフルオロエチレンとパーフルオロアルキルビニルエーテルとの共重合体(以下、PFAと称する。)は溶融可能なフッ素樹脂としてよく知られており、チューブ、パイプ、継手、容器等の成形品として、またコーティング、ライニング等に幅広く使用されている。特に半導体製造工程においては、その優れた耐薬品性、耐熱性からウエハーキャリヤーやボトルあるい 50

はチューブ等の配管の材料として広く用いられている。 【0003】

【発明が解決しようとする課題】しかしながら、PFAといえども詳細に見ればいくつかの問題点を有している。即ち、PFAは、溶出するパーティクルがポリエチレン等の汎用樹脂と比べると比較的多く、高集積LSI製造用の各種容器或いは治具として使用したときには歩留り悪化の原因となり、それ故パーティクルの低減が強く要求されている。

10 【0004】PFAをフロン-113で抽出した後の希フッ酸浸漬テストにおいてパーティクル発生量の経時的増加率が低下したことから、PFAから発生するパーティクルの原因の一つは、PFAに含まれるオリゴマーであると考えられている。そこで、パーティクル低減の方法として、PFA成形体の洗浄、フッ素ガス処理、成形時のエアーパージといった処理が試みられ、その結果パーティクルの初期発生量が低減されている(ウルトラクリーンテクノロジー第2巻456及び463ベージ、1990年)。しかしながら、これらの方法はいずれも表面の処理であり、経時的には樹脂内部からオリゴマーが溶出してくるため根本的な解決に至っていないのが現状である。

[0005]

【課題を解決するための手段】本発明者らは、パーティクルの発生量の少ない含フッ素樹脂、即ち、オリゴマー成分の少ない含フッ素樹脂について鋭意検討した結果、重合の終了時に重合停止剤を添加することによってオリゴマー含有量の極めて少ない含フッ素共重合体が得られることを見いだし、本発明を完成するに至った。

30 【0006】即ち、本発明は、一般式(I)

 $-(CF_{1}CF_{2})-(1)$

に基づく単量体単位90~99.5モル%および一般式 (II)

[0007]

[化3]

【0008】(但し、Rfはハロゲン化炭化水素基である。)で示される単量体単位10~0.5モル%からなり、372℃で測定した比溶融粘度が10°~10°ボイズであり、含フッ素有機溶媒での抽出による重量減少が0.01重量%以下であることを特徴とする含フッ素共重合体である。

【0009】また、本発明は、一般式(1)

 $-(CF_1CF_2)-(I)$

に基づく単量体単位60モル%以上90モル%未満および一般式(II)

[0010]

0 【化4】

,

- (CF₂ÇF) (Π)

【0011】(但し、Rfはハロゲン化炭化水素基であ る。)で示される単量体単位10モル%を越え40モル %以下からなり、200℃で測定した比溶融粘度が10 1~107ポイズであり、含フッ素有機溶媒での抽出によ る重量減少が0.01重量%以下であることを特徴とす る含フッ素共重合体である。

【0012】前記一般式(1)で示される単量体単位 は、テトラフルオロエチレンの重合に基づく単量体単位 である。

【0013】前記一般式(II)で示される単量体単位 中、Rfで示される基は一般にハロゲン化炭化水素基が 用いられるが、特に本発明において好適な基は、パーフ ルオロアルキル基、及び下記一般式(IV)

-CH2CaFbXcH(24+1-b-c) (IV)

(但し、Xは塩素原子または臭素原子であり、aは1以 上の整数であり、bは0~2a+1の整数であり、cは する。)で示される基である。Rfで示されるハロゲン 化炭化水素基の炭素数は特に制限されないが、原料の入 手の容易さから炭素数1~8であることが好ましい。

【0014】本発明においては、前記一般式(II)で示 される単量体単位のなかでも、Rfが一般式(IV)であ る場合に、本発明の含フッ素共重合体はオリゴマーの含 有量が少なく、且つ良好な引張破断強度を有するために 好適である。この理由については、後述する本発明の含 フッ素共重合体の製造方法において、Rfが一般式(I V) であるモノマーは、パーフルオロアルキル基である モノマーより重合性が良いため、モノマー除去段階にお けるオリゴマー成分の生成防止効果が大きいためである と考えることができる。

【0015】前記一般式(I)及び(II)で示される各 単量体単位の組成は、前記一般式(1)で示される単位 が60~99.5モル%であり、前記一般式(II)で示 される単位が40~0.5モル%である。前記一般式

(II)で示される単量体単位の量が上記の範囲よりも少 ないときは、溶融粘度が高くなりすぎ成形性の悪い共重 合体となり、逆に上記範囲よりも多いときは軟化温度が 40 低下するため成形性に問題が生じ好ましくない。本発明 の含フッ素共重合体の成形性を勘案すると、前記一般式 (I) および (II) で示される単量体単位は、それぞれ 75~99.5モル%および25~0.5モル%である ことが好ましく、さらに、それぞれ90~99モル%お よび10~1モル%であることが好ましい。

【0016】本発明の含フッ素共重合体は、前記一般式 (I) および (II) で示される単量体単位がランダムに 配列したランダム共重合体である。

不溶であるために通常の手段では分子量を求めることが できない。しかし、本発明の含フッ素共重合体の比溶融 粘度は分子量に依存しているために、比溶融粘度を測定 することによって分子量を推定することができる。即 ち、本発明の含フッ素共重合体のうち前記一般式(II) で示される単量体単位が0.5~10モル%の範囲であ る共重合体は、372℃で測定した比溶融粘度が102 ~10'ボイズの範囲となる。また、前記一般式 (II) で示される単量体単位が10モル%を越え40モル%以 下である共重合体は、200℃で測定した比溶融粘度が 10'~10'ボイズの範囲となる。比溶融粘度は、いず れの場合も共重合体の成形性を勘案すると、10'~1 0°ポイズの範囲であることが好ましい。

【0018】また、本発明の含フッ素共重合体は、J] S K-7113に基づいて測定された引張破断強度が 250kg/cm'以上であり、機械的強度においても 十分な物性を有している。上記の引張破断強度は、さら に300kg/cm'以上とすることもできる。

【0019】更に本発明の含ファ素共重合体中に含まれ 0又は1であり、且つ1≦b+c≦2a+1の関係を有 20 るオリゴマーは、含フッ素有機溶媒で抽出することがで き、含フッ素有機溶媒中で80℃、18時間、抽出後の 重量減少によって定量することができる。本発明の含フ ッ素共重合体は、含フッ素有機溶媒で抽出されたときの 重量減少率が0.01重量%以下であり、さらに0.0 08重量%以下とすることもできる。

> 【0020】含フッ素共重合体中のオリゴマーの抽出に 使用する含フッ素有機溶媒は、分子中にフッ素原子を有 する公知の有機溶媒を何等制限なく使用することができ る。特に本発明において好適に使用しうる含フッ素有機 30 溶媒を具体的に例示すると、例えば、CFC1,CF,C l (フロン-113)、CH,CC1,F (フロン-14 1 b) をあげることができる。

【0021】上記の含フッ素有機溶媒を用いて、本発明 の含フッ素共重合体と従来の含フッ素共重合体の重量減 少率を比較したところ、本発明の含フッ素共重合体の重 量減少は極めて低く、オリゴマー成分の含有量が少ない といえる。

【0022】本発明の含フッ素共重合体は、赤外吸収ス ベクトル(以下、単に IRという。)を測定することに より、その化学構造を確認することができる。即ち、前 記一般式(II)で示される単量体単位中、Rfがパーフ ルオロアルキル基の場合、990cm-1付近に>CFO CF,-基および1200cm⁻¹付近に-CF,-基に基 づく吸収帯を有しており、また、前記一般式 (II) で示 される単量体単位中、Rfが前記一般式(IV)で示され る基の場合、950cm゚゚付近に>CFOCH、-基お よび2900cm-1付近に-CHュー基に基づく吸収帯 を有している。

【0023】本発明の含フッ素共重合体は、どのような 【0017】本発明の含フッ素共重合体は、各種溶媒に 50 方法で製造されても良いが、特に次に述べる方法で好適

に製造される。

【0024】即ち、テトラフルオロエチレンと下記一般 式(III)

 $CF_i = CFORf$ (III)

(但し、Rfはハロゲン化炭化水素基である。)で示さ れる含フッ素ビニルエーテルを共重合させ、重合停止剤 を添加した後未反応モノマーの除去を行う方法である。 【0025】前記一般式 (III) 中のRfで示されるハ ロゲン化炭化水素基は、前記一般式(II)中のRfと同 般式(III)で示される含フッ素ピニルエーテルを具体 的に例示すると、

 $CF_1 = CFOCH_1CF_1$, $CF_2 = CFOCH_1CF_2$ CF_1 . CF_2 = $CFOCH_1CF_2CF_2H_1$. $CF_{1}=C$ FOCH, (CF,), CF, = CFOCH, (CF $(CF_1) CF_2 = CFOCH_1 (CF_2) CF_3 C$ $F_i = CFOCH_i$ (CF_i), CF_i, CF_i = CFOC $H_1(CF_1)_{\bullet}CF_{\bullet}, CF_{\bullet}=CFOCH_{\bullet}(CF_{\bullet})_{\bullet}C$ F_1 . $CF_2 = CFOCH_2CF_2CI_1$, $CF_2 = CFO$ $CH_1CF_2Br_1$ $CF_2=CFOCH_2CF_2CF_3C$ 1, $CF_2 = CFOCH_2CF_2CF_2Br$, $CF_2 = C$ FOCH, (CF,), CF, CI, CF, = CFOCH $(CF_1)_1CF_2Br, CF_1=CFOCH_1(CF_1)_1$ CF, C1, CF, = CFOCH, (CF,), CF, Br, $CF_1 = CFOCF_1$, $CF_2 = CFOCF_2CF_3$, C $F_1 = CFO(CF_1)_1CF_2$, $CF_2 = CFO(C$ F_2), CF_3 , CF_4 = $CFO(CF_4)$, CF_3 , CF_4 $=CFO(CF_1), CF_1, CF_2 = CFO(CF_1), C$ F_1 . $CF_2 = CFO(CF_1), CF_3, CF_4 = CFO$ (CF₁),CF,等をあげることができる。

【0026】本発明においてテトラフルオロエチレンと 前記一般式(III)で示される含フッ素ピニルエーテル の仕込み組成は、得られる含フッ素共重合体の溶融粘度 をあまり大きくせず、且つ軟化温度を適当な値に維持し て成形加工を容易にするためには、前記一般式(III) * **で示される含フッ素ビニルエーテルが0.5~40モル %、テトラフルオロエチレンが99.5~60モル%の 範囲であることが好ましく、さらに、前記一般式(II I) で示される含フッ素ビニルエーテルが0.5~25 モル%、テトラフルオロエチレンが99、5~75モル %の範囲であることが好ましい。

【0027】更にまた、得られる共重合体の性質を改質 するためにテトラフルオロエチレンにヘキサフルオロブ ロビレン、クロロトリフルオロエチレン、フッ化ビニリ 様の基を採用することができる。本発明で用いられる― 10 デン等のフルオロオレフィンを加えても良い。これらは 一般にテトラフルオロエチレンに対し5モル%以下用い るのが好ましい。

> 【0028】次に、上記含フッ素ビニルエーテルとテト ラフルオロエチレンとの共重合の方法は特に制限無く公 知の方法が採用される。即ち、溶液重合法、懸濁重合法 及び乳化重合法等の任意の方法が採用され、モノマーの 共重合性等の条件によって最適な重合方法を選択すれば

【0029】このうち、まず、溶液重合法について具体 20 的に説明すると、使用される重合溶媒は特に限定はされ ないが、一般にはクロロフルオロカーボン、クロロフル オロハイドロカーボン、パーフルオロカーボン等が好適 に用いられる。また、溶液重合の場合、重合熱の除去の ために重合溶媒中に0.3~10倍重量、好ましくは1 ~5倍重量の水を共存させて重合することも可能であ

【0030】また、重合開始剤としては、公知のラジカ ル発生剤が採用できるが、得られる共重合体の耐熱性を 考慮すると、含フッ素系ラジカル発生剤が好ましい。例 30 えば

 $(Z(CF_1),CO_1),$

(但し、Zは、水素原子、フッ素原子または塩素原子で あり、yは1~5の整数である。)

[0031]

[化5]

 $[Z(CF_2), (OCFCF_2), OCFCO_2]_2$ CF_3 CF_a

【0032】(但し、乙は、水素原子、フッ素原子また は塩素原子であり、yは1~5の整数であり、qは0~ 40 3の整数である。) が好適に使用できる。本発明におい て好適に使用されるラジカル発生剤の具体例を示せば、 $(HCF_1CF_1CO_1)_1$, $(CF_1CF_1CO_1)_1$ F, CF, CF, CO,) .. (CF, CF, CF, CF, C O_{i}), (CICF, CF, CO,), [0033]

> $(CF_3CF_2CF_2OCFCO_2)_2$ ĊFa

【化6】

【0034】を挙げることができる。

【0035】上記ラジカル発生剤の使用量は、用いる溶 媒、重合条件、特に温度によって一概には決定できない が、通常用いるモノマー量に対して0.002~0.5 モル%、好ましくは0.005~0.2モル%の範囲か ら選べば良い。また、ラジカル発生剤は重合開始時に一 括して導入しても良く、重合中に間歇的に導入しても良 い。特に、条件によっては途中重合が進み難い場合があ るが、このような場合、途中に再度ラジカル発生剤を追 加することは有効な手段である。

【0036】重合温度は用いるラジカル発生剤の分解速 50 度を一つの目安として決められるが、通常、0~100

℃、好ましくは5~60℃である。

【0037】次に懸濁重合について説明する。懸濁重合における重合開始剤、その使用量および重合温度は、上記溶液重合と同様に実施することができる。懸濁重合においては分散安定剤を使用することが好ましい。分散安定剤としては公知のものが何等制限なく採用されるが、パーフルオロカルボン酸アンモニウム、パーフルオロスルホン酸アンモニウム、ポリビニルアルコール等が用いられ、特に分散安定性の効果と、得られた含フッ素共重合体の熱安定性の点から炭素数が5~10の長鎖アルキル基を有するパーフルオロカルボン酸アンモニウムが好適である。また分散安定性の観点から上記分散安定剤の他にクロロフルオロカーボン、パーフルオロカーボンを用いても良く、その量は水に対して0.1~1倍重量が好適である。

【0039】いずれの重合方法においてもテトラフルオロエチレンの圧力は $1\sim30~k~g/c~m^i-G$ の範囲であれば充分に重合反応は進行するが、あまり高圧の場合は装置的にかなり高価となる欠点が生じてくるため、通常は $1\sim10~k~g/c~m^i-G$ が好ましい。

【0040】上記のモノマー成分の重合槽への供給につ 30 いては、所定量のテトラフルオロエチレンと含フッ素ビニルエーテルを重合槽に封じ込んで重合を行っても良く、また、テトラフルオロエチレンと含フッ素ビニルエーテルの重合による消費量に応じて、テトラフルオロエチレンと含フッ素ビニルエーテルのいずれか一方を、または両方を、重合中に連続的或いは間歇的に添加しても良い。

【0041】更に、いずれの重合方法においても分子量調節のために必要量の連鎖移動剤を添加することが好ましい。連鎖移動剤としては、四塩化炭素、クロロホルム 40等の塩素化炭化水素類;ヘキサン、ベンタン、ブタン、ブロバン、エタン、メタン等のアルカン類;ジエチルエーテル、ジメチルエーテル等のエーテル類:メタノール、エタノール等のアルコール類を用いることができるが、これらのうち重合溶媒への溶解量、及び生成した共重合体の安定性等の理由からアルカン類及びアルコール類が好ましい。連鎖移動剤が気体であれば重合溶媒への必要な溶解量を維持できる圧力で圧入すれば良い。また、液体であれば必要量を予め、又は間歇的に加えれば良い。連鎖移動剤の使用量は連鎖移動剤の種類 電合条 50

件によって若干の範囲で変動するが、通常、重合槽中の 全モノマー量に対して0.05~10モル%、好ましく は0.1~5モル%の範囲であることが好ましい。ここ で重合系に水が存在する場合は連鎖移動剤の水相と有機 相との分配比を考慮し、有機相における連鎖移動剤の濃 度が上記の範囲となるよう添加にすることが好ましい。 【0042】本発明の方法においては、上記の共重合を 行った後、重合停止剤を添加して重合反応を停止させ る。重合停止剤は、実質的に重合反応を停止させること ができる化合物であれば特に制限されず使用できる。具 体的には、メタノール、エタノール等のアルコール類; ヘキサン、ペンタン、ブタン等の炭化水素類;四塩化炭 素、クロロホルム等の塩素化炭化水素類;リモネン、シ メン、ビネン等のテルペン類:ベンゾキノン、ナフトキ ノン等のキノン類;ヒドロキノン、クレゾール、カテコ ール等のフェノール類を用いることができ、このうち重 合反応停止の効率、含フッ素共重合体からの分離、得ら れた含フッ素共重合体の熱安定性等の理由により、アル コール類、炭化水素類、塩素化炭化水素類が好適であ

【0043】重合停止剤の添加量は、重合方法、添加する重合停止剤の効率等によって一概には決定できないが、通常は、重合系に残存する未反応モノマー量に対して10モル%を越えて使用すれば十分であるが、重合反応停止の効率および本発明の含フッ素共重合体と重合停止剤との分離の観点等から20~300モル%の範囲が好ましい。

【0044】なお、未反応モノマーの残存量は、次のようにして求めることができる。例えば、未反応テトラフルオロエチレン量は反応器の圧力、温度および重合溶媒に対するテトラフルオロエチレンの溶解度から算出でき、未反応含フッ素ビニルエーテル量は反応器への導入量とテトラフルオロエチレンの消費量から概略見積もることができる。

【0045】重合停止剤の添加時期は、重合反応が始まった後であって重合系内に未反応モノマーが残存している状態であればどの段階でも効果がある。しかしながら、あまりにも重合の初期段階であると含フッ素共重合体の生産性の観点から不都合であり、また、あまり重合反応が進んで重合系が高粘度となった場合は均一な攪拌が困難となり、その結果重合熱の除去が不十分となって、得られる共重合体の物性に悪影響を与えることがある。従って、重合停止剤の添加時期は、得られる含フッ素共重合体の物性と生産性の観点から決定すれば良いが、通常、反応液中の含フッ素共重合体の濃度が2~30重量%、好ましくは3~20重量%の範囲となった時点であることが好ましい。

必要な溶解量を維持できる圧力で圧入すれば良い。ま 【0046】また、重合停止剤の添加方法は特には限定た、液体であれば必要量を予め、又は間歇的に加えれば はされないが、重合系に重合停止剤を圧入する方法、重良い。連鎖移動剤の使用量は連鎖移動剤の種類、重合条 50 合反応液を重合停止剤の入った容器に移送する方法、未

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反応テトラフルオロエチレンの放出による脱圧直後に重 合停止剤を導入する方法等が例として挙げられる。

【0047】本発明においては、重合停止剤の添加後に。未反応モノマーが除去される。未反応モノマーの除去は、未反応テトラフルオロエチレンと、未反応フルオロアルキルビニルエーテルの少なくとも一方を除去することであり、その操作は公知のモノマー除去方法を採用することができる。例えば、重合槽の気相からガス状のテトラフルオロエチレンを放出させる操作、重合溶媒中に溶解した未反応テトラフルオロエチレンおよび未反応フルオロアルキルビニルエーテルをろ過、遠心分離、加熱、減圧等の手段によって含フッ素共重合体と分離する操作等をあげることができる。

【0048】生成した含フッ素共重合体は、重合反応混合物から未反応モノマー、溶媒、余剰の重合停止剤等を分離して得られる。

【0049】本発明の含フッ素共重合体の内、分子内に水素原子を有するものは、フッ素化剤、例えば、F.を用いてフッ素化することにより、従来の炭化水素重合体のフッ素化で認められる主鎖の切断を起こすことなく高 20 収率でフッ素化することができ、パーフルオロ共重合体とすることができる。

[0050]

【発明の効果】本発明の含フッ素共重合体をフッ酸に浸漬し発生するパーティクルを測定したところ、初期の発生量が極めて少ないのみならず、時間経過後も増加することはない。また、フロンー113やフロンー141b等の含フッ素有機溶媒で抽出したときの重量減少が0.01重量%以下と極めて少ない。このことから、本発明の含フッ素共重合体は、オリゴマー成分の含有量が極めて少ないといえる。また、オリゴマー成分以外にもパーティクルの原因となる成分がフッ素樹脂には含まれていると考えられるが、本発明の含フッ素共重合体のパーティクル発生量が極めて低いことから、このようなオリゴマー以外のパーティクルの原因となるような成分も低減されていると考えられる。

【0051】また、本発明の含フッ素共重合体は機械的物性が優れており、従来の方法で製造した同一組成、同一比溶融粘度の共重合体より、通常30~60kg/cm²高い引張破断強度を有し、との点からも本発明は優れていると言える。

【0052】従って、本発明の含フッ素共重合体は、半導体製造工程においてウエハーキャリヤーやボトルあるいはチューブ等の配管システムに用いた場合、バーティクルの発生量が少なく、高集積LSIの製造において有効であるばかりでなく、機械強度の改良された含フッ素共重合体として耐薬品性、耐熱性、電気特性等フッ素樹脂としての特性が要求される産業分野において使用できる。

[0053]

【実施例】本発明を更に詳細に説明するために以下に実施例を示すが、本発明はこれら実施例によって何等制限をうけるものではない。

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【0054】なお、測定値は次のようにして求めた。

【0055】1.a. 引張破断強度の測定

JIS K-7113に準拠。

【0056】b. テストサンプルの作成

本発明の含フッ素共重合体及び比較のための樹脂を350°Cの温度で溶融し、加圧下冷却することによって、1mm厚のシートを作成し、上記試験法に必要な試験片を作成した。

【0057】2. 比溶融粘度の測定

高化式フローテスターを用いた。直径1mm、長さ10mmのダイスを用い、温度372℃で13.14kgの荷重で測定した

3. a. パーティクルの測定

試験片を高純度イソプロビルアルコール及び超純水で繰り返し洗浄し、クリーンルーム内で自然乾燥させた後、高純度50%フッ酸溶液500gに浸漬しパーティクル数の経時変化を測定した。なお測定にはパーティクルカウンターKL-22(リオン社製)を用い、0.3~2μmのパーティクル数をカウントした。

【0058】b、テストサンプルの作成

本発明の含フッ素共重合体及び比較のための樹脂を350℃の温度で溶融し、加圧下冷却することによって、1mm厚のシートを作成し、50mm×70mmに切り出して上記試験に必要な試験片を作成した。

【0059】実施例1

攪拌機を有したステンレス製の75L反応器に予め蒸留 により精製したフロン-113 45 kgを入れた後、 内部を脱気し、その後、窒素ガスで大気圧とした。反応 器内にメタノール6. 0gおよび2,2,3,3,3-ペンタフル オロプロピルトリフルオロビニルエーテル320gを入 れた後、攪拌モーターの回転数を140回転とし、テト ラフルオロエチレンを導入し圧力を4.2kg/cm² -Gにした。次いで反応器内を18℃に保ちつつ(C, F,CO,),のフロン-113溶液(5wt%)55. 3gを導入し重合を開始した。反応器圧力が2.6kg /cm²-G、生成した含フッ素共重合体の濃度が反応 40 液中に4. 4重量%になったところでメタノール850 8を入れて重合を停止させた。次に、反応器内の未反応 テトラフルオロエチレンを放出した後、反応液を攪拌機 を有する100Lのポリマー析出槽に移し、ポリマー析 出槽を加熱することにより重合溶媒および未反応モノマ ーを留出させ含フッ素共重合体を得た。この共重合体を 150℃で12時間真空乾燥したところ2kgの共重合 体が得られた。

【0060】 この含フッ素共重合体を330°Cでフィルム化して1Rを測定し、その結果を図1に示した。図1 50 において、950cm⁻¹付近に>CFOCH₂-基およ

び2900cm⁻¹付近に-CH₂-基に基づく吸収帯が確認され、含フッ素共重合体中に2,2,3,3,3-ベンタフルオロプロビルトリフルオロビニルエーテルに基づく単量・体単位が2.8モル%含まれていることがわかった。また、この重合体を溶融成形し、JIS K-7113に基づいて引張破断強度を測定したところ、440kg/cm²であった。また、372℃での比溶融粘度は1.5×10³ポイズであった。

【0061】更に、この重合体 1 k g を容量 3 L のオートクレーブに入れ、フロンー 1 1 3 およびフロンー 1 4 10 10 L のポリマー析出槽に移し、重合を停止させた。 1 b をそれぞれ 1 L 用い、80℃で 1 8 時間抽出を行った。 濾過によって共重合体と溶媒を分離した後、共重合体を150℃で 1 2 時間減圧乾燥した。このときの共重合体の重量減少はフロンー 1 1 3 で0、004重量%、フロンー 1 4 1 b で0、004重量%であった。また、 1 3 モル%であることがわかった。また、 引張破胎 4 g の白色物質が得られた。

【0062】比較例1

反応器圧力が2.6 kg/cm² になった後、メタノールを添加することなく未反応モノマー及び溶媒を留出さ 20 せた他は実施例1と同様にして反応を行った。分析の結果、得られた共重合体中には2,2,3,3,3-ペンタフルオロプロビルトリフルオロビニルエーテルに基づく単量体単位が2.8 モル%含まれていた。また、引張破断強度は380 kg/cm²であり、比溶融粘度は1.4×10³ ボイズであり、フロン-113で抽出後の重量減少は0.05 重量%であった。

【0063】さらに、フロン-113で抽出した共重合体を、再びフロン-113で抽出を行ったところ、重量減少は0.025重量%であった。また、この共重合体 30のフロン-141bでの抽出による重量減少は0.05重量%であった。

【0064】実施例2

攪拌機を有したステンレス製の75 L 反応器に予め蒸留 により精製したフロンー113 70 kgを入れた後、内部を脱気し、その後、窒素ガスで大気圧とした。オートクレーブ内にメタノール37g およびパーフルオロプロビルビニルエーテル6.2 kgを入れた後、攪拌モー

ターの回転数を140回転とし、テトラフルオロエチレンを導入し圧力を6kg/сm²ーGにした。次いで反応器内を18℃に保ちつつ(C,F,CO,)。のフロンー113溶液(5wt%)180gを導入し重合を開始した。反応器圧力が6kg/сm²ーGを維持するようテトラフルオロエチレンを連続的に供給した。テトラフルオロエチレンの供給量が3.9kg、生成した含フッ素共重合体の濃度が反応液中に6.7重量%になったところで反応液をメタノール1kgが入った撹拌機を有する100Lのポリマー析出槽に移し、重合を停止させた。次にポリマー析出槽を加熱することにより溶媒および未反応モノマーを留出させ共重合体を得た。

【0065】IR測定の結果、990cm⁻¹付近に>CFOCF₁-基および1200cm⁻¹付近に-CF₁-基に基づく吸収帯が確認され、この共重合体のパーフルオロプロビルビニルエーテルに基づく単量体単位の含有率は1.3 モル%であることがわかった。また、引張破断強度は410kg/cm²であり、372℃での比溶融粘度は8.0×10⁴ボイズであり、フロン-113 およびフロン-141 bで抽出後の重量減少はそれぞれ0.007重量%および0.008重量%であった。【0066】比較例2

ボリマー析出槽にメタノールを入れない他は実施例2と同様にして反応を行った。分析の結果、この共重合体のパーフルオロプロピルビニルエーテルに基づく単量体単位の含有率は1.3モル%であり、372℃での比溶融粘度は6.7×10⁴ボイズであり、引張破断強度は370kg/cm²、フロン-113で抽出後の重量減少は0.06重量%であった。

80 【0067】実施例3

実施例 1、 2 および比較例 1、 2 で得られた含フッ素共重合体をフロンー 1 1 3 で抽出した後の共重合体を 5 0%フッ酸中に浸漬し、フッ酸溶液 1 c c 中の 0. 3 \sim 2 μ m のパーティクル数を浸漬開始から 6、 9、 1 4 日後に測定した。その結果を表 1 に示した。

[0068]

【表1】

表 1

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	パーティクル	数(個/cc-	フッ酸溶液)
	8日後	9日後	14日後
実施例 1	8	8	8
比較例 1 (1回目7四抽出前)	390	5 2 5	700
比較例 1 (1回目702抽出後)	98	138	177
実施例 2	1 4	l 4	1 4
比較例 2	203	3 1 0	3 9 5

【0069】実施例4

攪拌機を有したステンレス製の75L反応器に予め蒸留 により精製したフロン-113 45kgを入れた後、 内部を脱気し、その後予め調製しておいた9モル%の2. 2,2-トリフルオロエチルトリフルオロビニルエーテルと 20 91モル%のテトラフルオロエチレンとの混合ガスを反 応器に導入し大気圧とした。反応器内にメタノール24 gを入れた後、攪拌モーターの回転数を140回転と し、上記混合ガスを導入して4.0kg/cm²-Gに した。次いで反応器内を22℃に保ちつつ(C,F,CO ,),のフロン-113溶液(5wt%)90gを導入し 重合を開始した。反応中上記混合ガスを連続的に導入し 4. 0 k g / c m² - Gを維持した。上記混合ガスの導 入量が3.0kg、生成した含フッ素共重合体の濃度が 反応液中に6.7重量%になったところでヘキサン1k gを入れて重合を停止させた後、実施例1と同様にして 共重合体を得た。

【0070】 I R測定の結果、実施例1と同様に、95 0 c m-1付近に>CFOCH, -基および2900 c m -1付近に-CH,-基に基づく吸収帯が認められ、共重 合体中に含まれる2,2,2-トリフルオロエチルトリフルオ ロビニルエーテルに基づく単量体単位は8.8モル%で あった。また、比溶融粘度は8. 0×10³ポイズであ り、引張破断強度は330kg/cm゚であり、フロン あった。

【0071】実施例5

攪拌機を有したステンレス製の75 L 反応器にイオン交 換水21kg、予め蒸留により精製したパーフルオロト yJJFhP = 15kg, C_1F_1 , CO_2NH_1OOg を入れた後、内部を脱気し、その後予め調製しておいた 3モル%の2,2,3,3,3-ペンタフルオロプロピルトリフル オロビニルエーテルと97モル%のテトラフルオロエチ レンとの混合ガスを反応器に導入し大気圧とした。反応 器内にエタノール5 kgを入れた後、攪拌モーターの回 50

転数を140回転とし、上記混合ガスを導入し4.0k g/cm'-Gにした。次いで反応器内を18℃に保ち つつ(CICF, CF, CO,), のパーフルオロトリプチ ルアミン溶液(5wt%)250gを導入し重合を開始 した。反応中上記混合ガスを連続的に導入し4.0kg /cm²-Gを維持した。上記混合ガスの導入量が2. 5 kg、生成した含フッ素共重合体の濃度が反応液中に 6. 9重量%になったところでクロロホルム1kgを入 れて重合を停止させた後、実施例 1 と同様にして共重合 体を得た。

【0072】IR測定の結果、実施例1と同様に、95 0 c m-1付近に>CFOCH2-基および2900 cm -1付近に-CH,-基に基づく吸収帯が認められ、共重 合体中に含まれる2,2,3,3,3-ペンタフルオロプロピルト 30 リフルオロビニルエーテルに基づく単量体単位は2.8 モル%であった。また、比溶融粘度は3.2×10°ボ イズであり、引張破断強度は460kg/cm²であ り、フロン-113による抽出の結果、重量減少は0. 003重量%であった。

【0073】実施例6

実施例1および2と同様な方法を用いて、種々の含フッ 素ビニルエーテルとテトラフルオロエチレンの反応を行 い、含フッ素共重合体を得た。用いた含フッ素ビニルエ ーテルの種類、重合停止剤、得られた共重合体中に含ま -113で抽出の結果、重量減少は0.005重量%で 40 れた含フッ素ビニルエーテルに基づく単量体単位の含有 量、および得られた共重合体の比溶融粘度、引張破断強 度、フロン-113での抽出による重量減少率、および 50%フッ酸に14日間浸漬後のパーティクル数を表2 に示した。

> 【0074】IR測定の結果、いづれの共重合体も実施 例1と同様に、950cm⁻¹付近に>CFOCH、-基 および2900cm-1付近に-CH、-基に基づく吸収 帯が認められた。

[0075]

【表2】

-	•

				表2					
ž	\$7. \$11111	重合作	重合停止剂	台7ッ米と"JAI-jA	比容融粘度	引張	707-113掛出	パ-ティタル数	
	B / J SR L - // L - // R	種類	(8) 曹	に移して単単年 単位(mol光)	(ボイズ)	級町類度 (kg/cm ³)	による国制減少率(%)	(四/四)	
-	CF2=CFOCH2CF2CF1	B0 * B3	1200	2.2	2.0×10 ⁴	460	0.001	2	
2	CFz=CFOCHz(CPz),CFs C4H10	C.H.	2000	5.0	1.2×104	350	0.004	7	
က	CF ₂ =CF0CH ₂ (CF ₂),CF ₃	CHC1,	1000	8 . 8	5.2×10°	320	0.008	7	
4	CF2=CFOCH2(CF2),CF1 CH2OH	CB ₂ OH	750	3. 1	1.4×10	360	0.005	9 *	
വ	CF2=CFOCH2CF2CF1C1	СН°вон	1000	3.0	1.2×10*	850	0.004	9	
ဖ	CFz=CFOCHzCFzCFrc1	но но	1000	1 2	9.5×10°*	320	0.007	14	
7	CF.=CPOCH, CF. CF. C1	B0 "B0	1000	2 1	3.3×104	300	0.008	2 1	
* (社	注)*印は200℃で測定した比溶融粘度であり、それ以外は372℃で測定した比溶融粘度である。	北洛融粘	度であり	、それ以外は37	2℃で選ぶし	た比容融格	度である。		

【図面の簡単な説明】

40 スペクトルのチャートである。

【図1】図1は、本発明の含フッ素共重合体の赤外吸収

> 2000 1800 1800 1400 1200 1000 800 Wavenumbers